DESCRIPTION

POLYIMIDE FILM

Technical Field

[0001]

The present invention relates to a polyimide film, particularly, a polyimide film preferable as a substrate for high frequency-matching electrical parts and superior in heat resistance.

Background Art

[0002]

As a material for substrates for electrical parts of information and telecommunication devices (broadcast devices, mobile radio, portable telecommunication devices etc.), radar, highspeed information processing devices and the like, ceramic has been conventionally used. Substrates made of ceramic have heat resistance and can also be used for recent information telecommunication devices having a high frequency signal band (reaching the GHz band). However, ceramic is not flexible and cannot be made thin, which limits its applicable field.

[0003]

Accordingly, consideration has been made as to the use of a film made of an organic material as a substrate for electrical parts, and a film made of polyimide and a film made of polytetrafluoroethylene have been proposed. The film made of polyimide has superior heat resistance and is strong, which enables advantageous provision of a thin film. On the other hand, problems of low signal strength, delay in signal transmission and the like are of concern in the application to high frequency signals. While the film made of polytetrafluoroethylene is also compatible with high frequency, it is associated with problems in that the film cannot be made thin due to low elastic modulus, the film shows poor adhesion to a metal

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conductor, a resistor and the like on the surface, the film is unsuitable for the production of ultrafine wiring circuits due to its high coefficient of linear thermal expansion which causes marked dimensional

5 changes due to temperature change, and the like. As a result, its applicable field is limited. As the situation stands, a film for a substrate, which can simultaneously achieve heat resistance, applicability to high frequency and flexibility, has not been obtained.

10 In addition, as a polyimide film having a high elastic modulus, a polyimide benzoxazole film made of polyimide having a benzoxazole ring in the main chain has been proposed (see patent reference 1). A print wiring board with the polyimide benzoxazole film as a

15 dielectric layer has also been proposed (see patent reference 2, patent reference 3).

patent reference 1 JP-A-6-56992

patent reference 2 JP-A-11-504369

patent reference 3 JP-A-11-505184

20 [0004]

As compared to conventional polyimide films, the polyimide benzoxazole film is also superior in the heat resistance. Thus, the curling developed during heat processing tends to be suppressed. However, further

25 improvements have been desired as electronics are miniaturized and the wiring becomes highly dense. In the application to ultrahigh frequency reaching the milliwave region, moreover, use of even a substrate made of a conventionally reported polyimide benzoxazole film

30 is inferior to the use of a substrate made of ceramic. To be precise, since the properties of the film vary markedly in response to humidity, the efficiency of high frequency signal transmission is low, and the response speed is low (poor rise of pulse signals), speeding up

35 of the operation of circuits made of a polyimide film is

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not easy, and further improvements are desired.

Disclosure of the Invention

Problems to be Solved by the Invention

[0005]

The present invention aims at providing a film made of an organic material with electronic property, particularly small humidity dependency, which maintains higher levels of heat resistance, applicability to high frequency and flexibility. In particular, the present invention aims at providing a polyimide film superior in thermal degradation stability, which is free of inconveniences due to curling even when various functional layers are laminated with heating.

Means of Solving the Problems

[0006]

The present inventors have conducted intensive studies and found that the dielectric loss tangent of a polyimide film can be unprecedentedly lowered by forming a particular higher order structure, and that such polyimide film simultaneously has heat resistance, applicability to high frequency and flexibility, which resulted in the completion of the present invention.

Accordingly, the present invention provides the following.

(1) A polyimide film obtainable by reacting an aromatic diamine with an aromatic tetracarbonic acid anhydride, which has a planar orientation coefficient of 0.79-0.89 as measured by the X-ray diffraction method, and a dielectric constant of 2.7-3.1 at 100 GHz as measured by a cavity resonance perturbation method.

(2) The polyimide film of claim 1, having a dielectric loss tangent at 100 GHz of 0.0001-0.03 as measured by the cavity resonance perturbation method.

(3) The polyimide film of claim 1 or 2, having dielectric constants of 2.7-3.1 at 1 GHz and 2.6-3.0 at

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100 GHz, as measured by the cavity resonance perturbation method.

(4) The polyimide film of any of claims 1 to 3, which has a density of 1.47 g/cm^3 – 1.55 g/cm^3.

(5) A polyimide film obtainable by reacting an aromatic diamine with an aromatic tetracarbonic acid anhydride, wherein the amount of water vaporized at a high temperature during heating at 500°C for 10 sec of the film immediately after helium purge at 170°C for 7 min and preliminary drying is not more than 5000 ppm.

(6) The polyimide film of any of claims 1 to 5, wherein the ratio ($\varepsilon_{65}/\varepsilon_D$) of the dielectric constant ε_{65} at 100 GHz of the film humidity-conditioned under the constant temperature and humidity conditions of 20°C, 65% RH for 94 hr, as measured by a cavity resonance perturbation method, to the dielectric constant εD at 100 GHz of the film vacuum dried under the conditions of 120°C for 24 hr, as measured by a cavity resonance perturbation method, is within the range of 1.00-1.10.

(7) A polyimide film obtainable by reacting an aromatic diamine with an aromatic tetracarbonic acid anhydride, wherein the absolute value of the difference between the surface planar orientation degree of one surface (surface A) and the surface planar orientation degree of the other surface (surface B) of the film is 0-2.

(8) The polyimide film of any of claims 1 to 7, wherein the surface planar orientation degree of a surface having a higher surface planar orientation degree is not more than 15.

(9) The polyimide film of any of claims 1 to 8, which has a curling degree of 0%-5%.

(10) The polyimide film of any of claims 1 to 9, wherein the aromatic diamine has a benzoxazole structure.

(11) A base substrate for printed wiring assemblies, which comprises the polyimide film of any of claims 1 to

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10.

(12) A method of producing a polyimide film, which comprises reacting an aromatic diamine with an aromatic tetracarbonic acid anhydride to give polyamide acid, casting a solution thereof on a support and drying the solution and the like to give a self-supporting polyimide precursor film (green film) and polyimidating said precursor film, wherein the polyimide precursor film (green film) satisfies all the relationships shown by the following formulas between an imidation rate Aim of one surface side (surface A side) and an imidation rate Bim of the other surface side (surface B side) of the polyimide precursor film (green film) and said polyimide precursor film is subjected to imidation.

formula 1; $|Aim-Bim| \leq 5$

formula 2; $0 \leq Aim \leq 15$

formula 3; $0 \leq Bim \leq 15$

Effect of the Invention

[0007]

The polyimide film of the present invention shows lower loss and faster response speed (good rise of pulse signals) at high frequency as compared to conventionally known polyimide films. Therefore, a circuit comprising the polyimide film of the present invention is expected to operate at a higher speed. In addition, it simultaneously has higher rigidity, strength and heat resistance than those of conventional polyimide films. Therefore, the film is preferably used for high frequency electronics and other electronics, and is useful as a substrate film for the production of copper-adhered substrates for flexible print circuit (FPC) with high size precision requirements, a carrier tape for tape automated bonding (TAB) and the like.

According to the present invention, for example, the difference in the surface planar orientation degree

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between the front and the back of the polyimide film is reduced by controlling the production conditions for obtaining a polyamide acid film from a polyamide acid solution and then imidating the polyamide acid film,

whereby an unprecedented polyimide film superior in thermal degradation stability, which has a curling degree of not more than 5% can be obtained. Moreover, the film of the present invention shows the dielectric constant ratio between a dry film and a wet film within a certain range as compared to conventionally known polyimide films. Therefore, a circuit comprising the film of the present invention is expected to afford operation with low humidity dependency. In addition, since a polyimide film wherein the amount of water evaporated at a high temperature is extremely small can be obtained, the development of swelling and delamination can be prevented even when used as a substrate film for various electrical laminate parts at a high temperature.

Best Mode for Embodying the Invention
[0008]

The embodiment of the polyimide film of the present invention is explained in detail in the following.

The polyimide film of the present invention is made of polyimide obtainable by reacting aromatic diamines with aromatic tetracarbonic acid anhydrides, and has a particular higher-order structure, particular dielectric property or a particular curling degree.

The aforementioned "reacting" includes first subjecting diamines and tetracarbonic acid anhydrides to an open ring polyaddition reaction in a solvent to give a polyamide acid solution, then forming a green film and the like as necessary from the polyamide acid solution and subjecting the film to dehydrocondensation (imidation).

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[0009]

As the aromatic diamines, for example, 4,4'-bis(3-aminophenoxy)biphenyl, bis[4-(3-aminophenoxy)phenyl]ketone, bis[4-(3-aminophenoxy)phenyl]sulfide, bis[4-(3-aminophenoxy)phenyl]sulfone, 2,2-bis[4-(3-aminophenoxy)phenyl]propane, 2,2-bis[4-(3-aminophenoxy)phenyl]-1,1,1,3,3,3-hexafluoropropane, m-phenylenediamine, o-phenylenediamine, p-phenylenediamine, m-aminobenzylamine, p-aminobenzylamine, 3,3'-diaminodiphenylether, 3,4'-diaminodiphenylether, 4,4'-diaminodiphenylether, 3,3'-diaminodiphenylsulfide, 3,3'-diaminodiphenylsulfoxide, 3,4'-diaminodiphenylsulfoxide, 4,4'-diaminodiphenylsulfoxide, 3,3'-diaminodiphenylsulfone, 3,4'-diaminodiphenylsulfone, 4,4'-diaminodiphenylsulfone, 3,3'-diaminobenzophenone, 3,4'-diaminobenzophenone, 4,4'-diaminobenzophenone, 3,3'-diaminodiphenylmethane, 3,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylmethane, bis[4-(4-aminophenoxy)phenyl]methane, 1,1-bis[4-(4-aminophenoxy)phenyl]ethane, 1,2-bis[4-(4-aminophenoxy)phenyl]ethane, 1,1-bis[4-(4-aminophenoxy)phenyl]propane, 1,2-bis[4-(4-aminophenoxy)phenyl]propane, 1,3-bis[4-(4-aminophenoxy)phenyl]propane, 2,2-bis[4-(4-aminophenoxy)phenyl]propane, 1,1-bis[4-(4-aminophenoxy)phenyl]butane, 1,3-bis[4-(4-aminophenoxy)phenyl]butane,

[0010]

1,4-bis[4-(4-aminophenoxy)phenyl]butane, 2,2-bis[4-(4-aminophenoxy)phenyl]butane, 2,3-bis[4-(4-aminophenoxy)phenyl]butane, 2-[4-(4-aminophenoxy)phenyl]-2-[4-(4-aminophenoxy)-3-methylphenyl]propane, 2,2-bis[4-(4-aminophenoxy)-3-

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methylphenyl]propane, 2-[4-(4-aminophenoxy)phenyl]-2-[4-
(4-aminophenoxy)-3,5-dimethylphenyl]propane, 2,2-bis[4-
(4-aminophenoxy)-3,5-dimethylphenyl]propane, 2,2-bis[4-
(4-aminophenoxy)phenyl]-1,1,1,3,3,3-hexafluoropropane,

5 1,4-bis(3-aminophenoxy)benzene, 1,3-bis(3-
aminophenoxy)benzene, 1,4-bis(4-aminophenoxy)benzene,
4,4'-bis(4-aminophenoxy)biphenyl, bis[4-(4-
aminophenoxy)phenyl]ketone, bis[4-(4-
aminophenoxy)phenyl]sulfide, bis[4-(4-

10 aminophenoxy)phenyl]sulfoxide, bis[4-(4-
aminophenoxy)phenyl]sulfone, bis[4-(3-
aminophenoxy)phenyl]ether, bis[4-(4-
aminophenoxy)phenyl]ether, 1,3-bis[4-(4-
aminophenoxy)benzoyl]benzene, 1,3-bis[4-(3-

15 aminophenoxy)benzoyl]benzene, 1,4-bis[4-(3-
aminophenoxy)benzoyl]benzene, 4,4'-bis(3-
aminophenoxy)benzoyl]benzene, 1,1-bis[4-(3-
aminophenoxy)phenyl]propane, 1,3-bis[4-(3-
aminophenoxy)phenyl]propane, 3,4'-

20 diaminodiphenylsulfide,
[0011]
2,2-bis[3-(3-aminophenoxy)phenyl]-1,1,1,3,3,3-
hexafluoropropane, bis[4-(3-aminophenoxy)phenyl]methane,
1,1-bis[4-(3-aminophenoxy)phenyl]ethane, 1,2-bis[4-(3-

25 aminophenoxy)phenyl]ethane, bis[4-(3-
aminophenoxy)phenyl]sulfoxide, 4,4'-bis[3-(4-
aminophenoxy)benzoyl]diphenylether, 4,4'-bis[3-(3-
aminophenoxy)benzoyl]diphenylether, 4,4'-bis[4-(4-amino-
α,α-dimethylbenzyl)phenoxy]benzophenone, 4,4'-bis[4-(4-

30 amino-α,α-dimethylbenzyl)phenoxy]diphenylsulfone, bis[4-
{4-(4-aminophenoxy)phenoxy}phenyl]sulfone, 1,4-bis[4-(4-
aminophenoxy)phenoxy-α,α-dimethylbenzyl]benzene, 1,3-
bis[4-(4-aminophenoxy)phenoxy-α,α-
dimethylbenzyl]benzene, 1,3-bis[4-(4-amino-6-

35 trifluoromethylphenoxy)-α,α-dimethylbenzyl]benzene, 1,3-

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bis[4-(4-amino-6-fluorophenoxy)-α,α-
dimethylbenzyl]benzene, 1,3-bis[4-(4-amino-6-
methylphenoxy)-α,α-dimethylbenzyl]benzene, 1,3-bis[4-(4-
amino-6-cyanophenoxy)-α,α-dimethylbenzyl]benzene, 3,3'-
diamino-4,4'-diphenoxybenzophenone, 4,4'-diamino-5,5'-
diphenoxybenzophenone, 3,4'-diamino-4,5'-
diphenoxybenzophenone, 3,3'-diamino-4-
phenoxybenzophenone, 4,4'-diamino-5-phenoxybenzophenone,
3,4'-diamino-4-phenoxybenzophenone, 3,4'-diamino-5'-
phenoxybenzophenone,

[0012]

3,3'-diamino-4,4'-dibiphenoxybenzophenone, 4,4'-diamino-
5,5'-dibiphenoxybenzophenone, 3,4'-diamino-4,5'-
dibiphenoxybenzophenone, 3,3'-diamino-4-
biphenoxybenzophenone, 4,4'-diamino-5-
biphenoxybenzophenone, 3,4'-diamino-4-
biphenoxybenzophenone, 3,4'-diamino-5'-
biphenoxybenzophenone, 1,3-bis(3-amino-4-
phenoxybenzoyl)benzene, 1,4-bis(3-amino-4-
phenoxybenzoyl)benzene, 1,3-bis(4-amino-5-
phenoxybenzoyl)benzene, 1,4-bis(4-amino-5-
phenoxybenzoyl)benzene, 1,3-bis(3-amino-4-
biphenoxybenzoyl)benzene, 1,4-bis(3-amino-4-
biphenoxybenzoyl)benzene, 1,3-bis(4-amino-5-
biphenoxybenzoyl)benzene, 1,4-bis(4-amino-5-
biphenoxybenzoyl)benzene, 2,6-bis[4-(4-amino-α,α-
dimethylbenzyl)phenoxy]benzonitrile, aromatic diamines
having a benzoxazole structure, and the above-mentioned
aromatic diamines wherein the hydrogen atoms on the
aromatic ring are partially or entirely substituted by a
halogen atom, an alkyl group or alkoxy group having 1 to
3 carbon atoms, a cyano group, or a halogenated alkyl
group or alkoxy group having 1 to 3 carbon atoms,
wherein the hydrogen atoms of the alkyl group or alkoxy
group are partially or entirely substituted by a halogen

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atom, and the like can be mentioned.

The aromatic diamines can be used alone or two or more kinds thereof can be used.

[0013]

Particularly, since a polyimide film superior in heat resistance, strength and rigidity can be obtained, aromatic diamines having a benzoxazole structure are preferable. As the aromatic diamines having a benzoxazole structure, the following can be concretely mentioned.

[0014][formula 1]

5-amino-2-(p-aminophenyl)benzoxazole
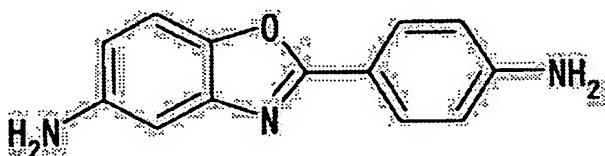
[0015][formula 2]

6-amino-2-(p-aminophenyl)benzoxazole
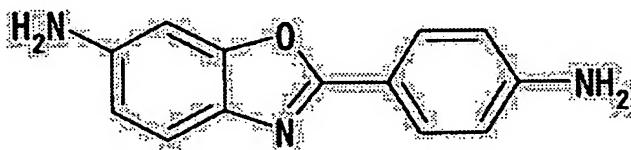
[0016][formula 3]

5-amino-2-(m-aminophenyl)benzoxazole
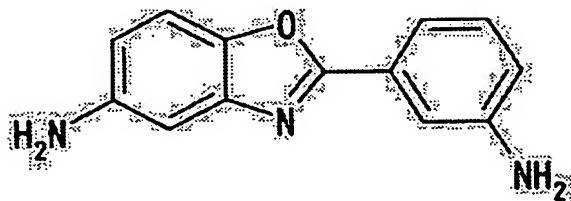
[0017][formula 4]

6-amino-2-(m-aminophenyl)benzoxazole

10
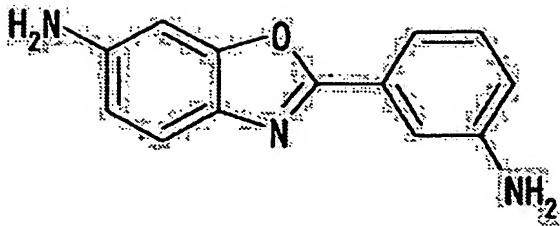
[0018] [formula 5]

2,2'-p-phenylenebis(5-aminobenzoxazole)
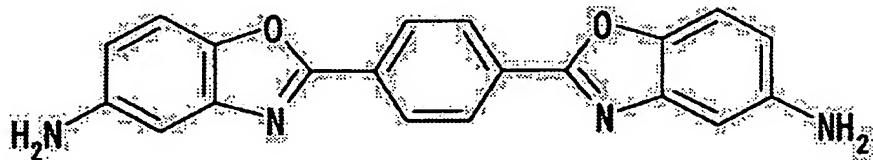
[0019] [formula 6]

2,2'-p-phenylenebis(6-aminobenzoxazole)
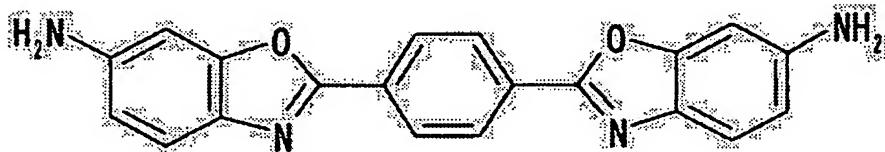
[0020] [formula 7]

1-(5-aminobenzoxazolo)-4-(6-aminobenzoxazolo)benzene
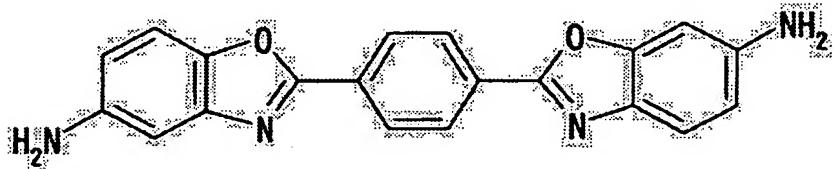
[0021] [formula 8]

2,6-(4,4'-diaminodiphenyl)benzo[1,2-d:5,4-d']bisoxazole
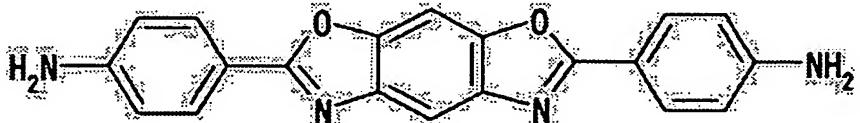
[0022] [formula 9]

2,6-(4,4'-diaminodiphenyl)benzo[1,2-d:4,5-d']bisoxazole

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[0023][formula 10]

2,6-(3,4'-diaminodiphenyl)benzo[1,2-d:5,4-d']bisoxazole
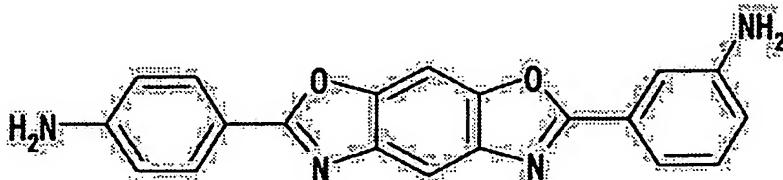
5

[0024][formula 11]

2,6-(3,4'-diaminodiphenyl)benzo[1,2-d:4,5-d']bisoxazole
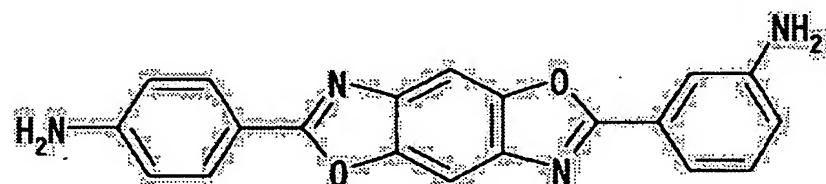
10 [0025][formula 12]

2,6-(3,3'-diaminodiphenyl)benzo[1,2-d:5,4-d']bisoxazole
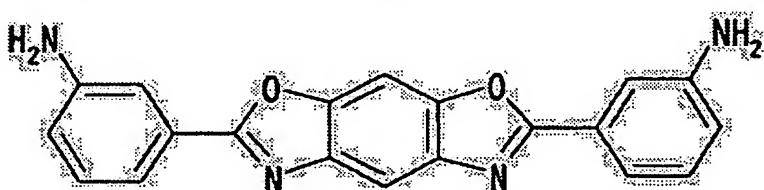
[0026][formula 13]

15 2,6-(3,3'-diaminodiphenyl)benzo[1,2-d:4,5-d']bisoxazole
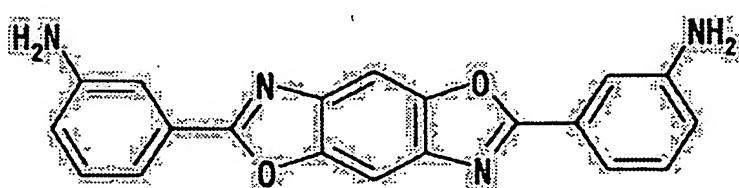
[0027]

    Of these, respective isomers of

20 amino(aminophenyl)benzoxazole are preferable in view of

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easiness of synthesis. As used herein, the "respective isomers" are those determined by the positions of the two amino groups of amino(aminophenyl)benzoxazole (e.g., respective compounds of the above-mentioned "formula 1"-

5 "formula 4").

[0028]

The tetracarbonic acid anhydrides to be used in the present invention are aromatic tetracarbonic acid anhydrides. As the aromatic tetracarbonic acid

10 anhydrides, the following can be concretely mentioned.

[0029][formula 14]
pyromellitic acid anhydride
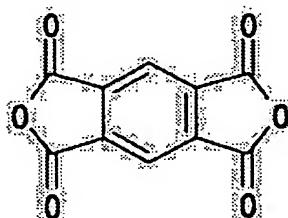
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[0030][formula 15]
3,3',4,4'-biphenyltetracarbonic acid anhydride
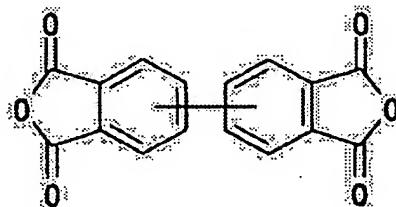
20 [0031][formula 16]
4,4'-oxydiphthalic acid anhydride

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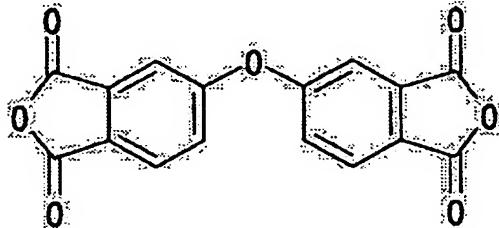
[0032] [formula 17]

3,3',4,4'-benzophenonetetracarbonic acid anhydride
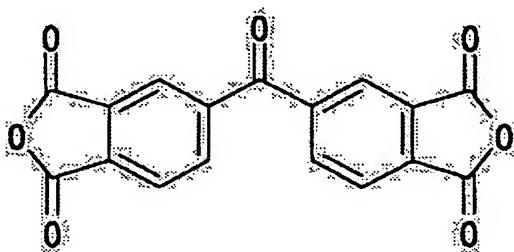
[0033] [formula 18]

3,3',4,4'-diphenylsulfonetetracarbonic acid anhydride
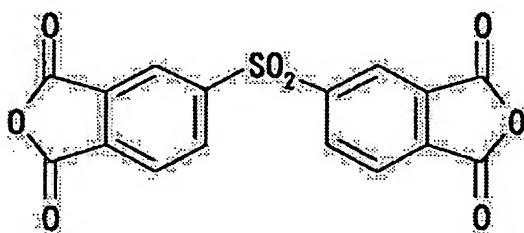
[0034] [formula 19]

2,2-bis[4-(3,4-dicarboxyphenoxy)phenyl]propanoic acid
anhydride
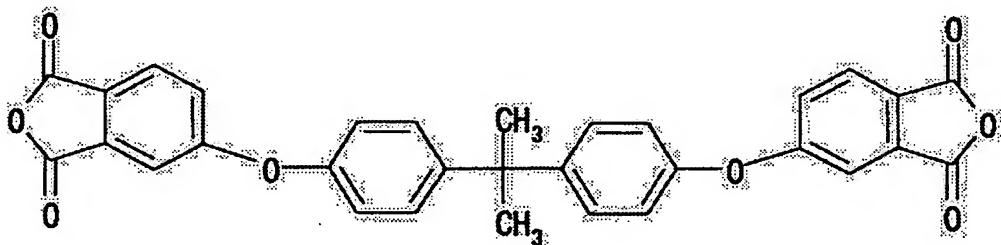
[0035]

     The aromatic tetracarbonic acid anhydrides can be
used alone or two or more kinds thereof can be used.

     In the present invention, one or more kinds of the
nonaromatic tetracarboxylic acid dianhydrides
exemplified below may be concurrently used as long as
their content is not more than 30 mol% of the total
tetracarboxylic acid dianhydride. As the nonaromatic
tetracarboxylic acid dianhydrides to be used, for

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example, butane-1,2,3,4-tetracarboxylic acid dianhydride,
pentane-1,2,4,5-tetracarboxylic acid dianhydride,
cyclobutanetetracarboxylic acid dianhydride,
cyclopentane-1,2,3,4-tetracarboxylic acid dianhydride,
5 cyclohexane-1,2,4,5-tetracarboxylic acid dianhydride,
cyclohex-1-ene-2,3,5,6-tetracarboxylic acid dianhydride,
3-ethylcyclohex-1-ene-3-(1,2),5,6-tetracarboxylic acid
dianhydride, 1-methyl-3-ethylcyclohexane-3-(1,2),5,6-
tetracarboxylic acid dianhydride, 1-methyl-3-
10 ethylcyclohex-1-ene-3-(1,2),5,6-tetracarboxylic acid
dianhydride, 1-ethylcyclohexane-1-(1,2),3,4-
tetracarboxylic acid dianhydride, 1-propylcyclohexane-1-
(2,3),3,4-tetracarboxylic acid dianhydride, 1,3-
dipropylcyclohexane-1-(2,3),3-(2,3)-tetracarboxylic acid
15 dianhydride, dicyclohexyl-3,4,3',4'-tetracarboxylic acid
dianhydride, bicyclo[2.2.1]heptane-2,3,5,6-
tetracarboxylic acid dianhydride, 1-propylcyclohexane-1-
(2,3),3,4-tetracarboxylic acid dianhydride, 1,3-
dipropylcyclohexane-1-(2,3),3-(2,3)-tetracarboxylic acid
20 dianhydride, dicyclohexyl-3,4,3',4'-tetracarboxylic acid
dianhydride, bicyclo[2.2.1]heptane-2,3,5,6-
tetracarboxylic acid dianhydride, bicyclo[2.2.2]octane-
2,3,5,6-tetracarboxylic acid dianhydride,
bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic acid
25 dianhydride and the like can be mentioned. The
nonaromatic tetracarboxylic acid dianhydrides can be
used alone or two or more kinds thereof can be used.
[0036]
         The polyimide film of the present invention can
30 contain a so-called lubricant for forming ultrafine
concaves and convexes on the film surface. As the
lubricant, fine particles of an organic compound and/or
an inorganic compound, which have an average particle
size of about 0.01-5 μm can be used. The amount of the
35 lubricant to be added is about 0.01-3% by mass of the

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mass of the film. In the present invention, highly heat resistant inorganic particles are preferably used, and metal oxide particles such as alumina, silica, titanium oxide and the like are more preferably used.

[0037]

The polyimide film of the present invention is produced by (a) first condensing aromatic diamines and aromatic tetracarbonic acid anhydrides in a solvent to give a polyamide acid solution (hereinafter to be referred to as Step (a)), then, (b) applying the polyamide acid solution to a support and drying the solution to afford self-supportiveness, which is specifically drying under the conditions to achieve the amount of the residual solvent relative to the total mass after drying of 25-50% by mass, to give a polyimide precursor film (also referred to as a green film) (hereinafter to be also referred to as step (b)), then, (c) heat treating the green film at a maximum temperature of 100-500°C to allow imidation reaction (hereinafter to be referred to as step (c)).

[0038]

In the above-mentioned steps (a)-(c), the film (including the green film) may be subjected to a stretching treatment where necessary, the area magnification ratio is preferably not more than 9, more preferably not more than 5, still more preferably not more than 2, and a non-stretch film free of a stretching treatment is further preferable. The non-stretch film here means a film obtained without drawing that intentionally applies a mechanical outer force such as tenter stretching, roll stretch, inflation stretch and the like. Too high an area magnification ratio is not preferable because the surface planar orientation degree of the polyimide film becomes too high, which makes it difficult to control the difference in the surface

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planar orientation degree between the front and the back of the film to fall within a given range, and the film is susceptible to the effect of change in the orientation due to a heat treatment (e.g., not less than 300°C).

[0039]

The production method of the polyimide film of the present invention (hereinafter to be simply referred to as the production method of the present invention) is explained in detail in the following.

[0040]

Step (a)

The solvent used for polymerizing aromatic diamines and aromatic tetracarbonic acid anhydrides to give polyamide acid is not particularly limited as long as it can dissolve any of the monomers to be the starting materials and the resulting polyamide acid. Preferred are polar organic solvents and, for example, N-methyl-2-pyrrolidone, N-acetyl-2-pyrrolidone, N,N-dimethylformamide, N,N-diethylformamide, N,N-dimethylacetamide, dimethyl sulfoxide, hexamethylphosphoric amide, ethyl cellosolveacetate, diethyleneglycoldimethylether, sulforane, halogenated phenols and the like can be mentioned. These solvents can be used alone or in a mixture. The amount of the solvent to be used is any as long as it is sufficient to dissolve monomers to be the starting materials. As a concrete amount to be used, an amount that affords generally 5-40% by mass, preferably 10-30% by mass, of the monomers in the solution dissolving the monomers can be mentioned.

[0041]

The conditions for the polymerization reaction (hereinafter to be also simply referred to as "polymerization reaction") to obtain polyamide acid may

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be conventionally known ones, and a specific example includes continuous stirring and/or mixing in an organic solvent within a temperature range of 0-80°C for 10 min - 80 hr. Where necessary, the polymerization reaction may be divided, pressure may be applied or the temperature may be increased or decreased. In this case, while the order of addition of both monomers is not particularly limited, addition of aromatic tetracarbonic acid anhydrides to a solution of aromatic diamines is preferable. The mass of polyamide acid in the polyamide acid solution obtained by the polymerization reaction is preferably 5-40% by mass, more preferably 10-30% by mass, and the viscosity of the aforementioned solution is preferably 10-2000 Pa·s, more preferably 100-1000 Pa·s, as measured by a Brook Field viscometer (25°C) in view of feeding stability.

[0042]

Vacuum defoaming during the polymerization reaction is effective to produce a good-quality organic solvent solution of polyamide acid. In addition, polymerization may be controlled by adding a small amount of a terminal sequestering agent to aromatic diamines before the polymerization reaction. As the terminal sequestering agent, a compound having a carbon -carbon double bond such as maleic anhydride and the like can be mentioned. The amount of maleic anhydride to be used is preferably 0.001-1.0 mol per 1 mol of the aromatic diamines.

[0043]

<Step (b)>

The support to be coated with a polyamide acid solution only needs to have smoothness and rigidity of the level sufficient to form a polyamide acid solution into a film-like product and, for example, a drum or belt-like rotation member having a surface made of a metal, plastic, glass, porcelain and the like, and the

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like can be mentioned. A method utilizing a polymer film having adequate rigidity and high smoothness is also a preferable embodiment. Particularly, the surface of the support is preferably a metal, more preferably stainless which is rustproof and superior in corrosion resistance. The surface of the support may be subjected to metal plating with Cr, Ni, Sn and the like. The surface of the support may be mirror-like or pearskin finished as necessary. A polyamide acid solution can be applied to a support by casting from a spinneret with a slit, extrusion from an extruder, squeeze coating, reverse coating, die coating, applicator coating, wire-bar coating and the like. Besides these, a conventionally known solution application means can be used appropriately.

[0044]

As a support to replace the above-mentioned, metal plates (foil, film, plate) can be mentioned. To be specific, as one production method of the below-mentioned polyimide film to be used for the production of a base substrate for a printed wiring assembly, a metal plate to be a metal layer of the aforementioned base substrate is used as a support and coated with a polyamide acid solution. In this case, the application means of the polyamide acid solution is not particularly limited, and known application means such as comma coater, knife coater, roll coater, reverse coater, die coater, gravure coater, wire-bar and the like can be mentioned.

[0045]

In Step (b), the amount of the residual solvent relative to the total mass (% by mass) of the obtained green film is preferably not more than 50% by mass, more preferably not more than 40% by mass, even more preferably not more than 35% by mass. When the amount of

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the residual solvent is greater than 50% by mass, the handling property becomes unpreferably degraded. While the lower limit of the amount of the residual solvent is not particularly limited, it is preferably not less than 25% by mass, more preferably not less than 30% by mass, to prevent film breakage during the imidation reaction step. The amount of the residual solvent can be measured (calculated) by TGA (thermogravimetric analysis), gel penetration chromatograph (GPC) and the like.

[0046]

To obtain a green film (self-supporting film made from a polyamide acid solution) wherein the amount of the residual solvent relative to the total mass of the film is within a given range, as the drying conditions when, for example, N,N-dimethylacetamide or N-methylpyrrolidone is used as a solvent, the drying temperature is preferably 70-130°C, more preferably 75-125°C, further preferably 80-120°C. When the drying temperature is higher than 130°C, the molecular weight decreases and the green film tends to be brittle. In addition, during the green film production, the imidation partly proceeds and the desired physical properties cannot be obtained easily during the imidation step. When the temperature is lower than 70°C, the drying time tends to be long, the molecular weight easily decreases and the handling property may be degraded due to insufficient drying. While the drying time varies depending on the drying temperature, it is preferably 10-90 min, more preferably 15-80 min. When the drying time is longer than 90 min, the molecular weight decreases and the film tends to be brittle. When it is shorter than 10 min, the handling property may be degraded due to insufficient drying. Moreover, for the improvement of the drying efficiency or for the suppression of the development of bubbles during drying,

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the temperature may be stepwisely raised within the range of 70-130°C to dry the film. As a dryer to achieve such conditions, a conventionally known dryer can be employed, and hot air, hot nitrogen, far infrared, high
5 frequency induction heating and the like can be mentioned.

In the case of hot air drying, to achieve not more than a given level of a difference in the surface planar orientation degree between the front and the back of a
10 green film during drying thereof to confer self-supportedness, the temperature difference between the upper face/lower face of the support is preferably controlled to not more than 10°C, preferably not more than 5°C. The temperature difference can be easily
15 controlled by individually controlling the hot air temperatures of the upper face/lower face.
[0047]

<Step (c)>

The green film obtained in Step (b) is imidated
20 under given conditions to give a polyimide film.

As a concrete method of imidation, a conventionally known imidation reaction can be appropriately employed. For example, a method comprising, where necessary, conducting a stretch treatment using a polyamide acid
25 solution free of a ring closing catalyst and a dehydrating agent, and then applying a heat treatment to allow progress of an imidation reaction (i.e., thermal ring closure method) and a chemical ring closure method comprising adding a ring closing catalyst and a
30 dehydrating agent to a polyamide acid solution, and allowing an imidation reaction to be carried out by the action of the above-mentioned ring closing catalyst and the dehydrating agent can be mentioned.

The present inventors have obtained a new finding
35 that particular imidation reaction conditions can adjust

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the planar orientation coefficient of the obtained film
to a particular value, as well as a new finding that the
film density can be controlled by subjecting the green
film peeled off from the support to annealing before
imidation treatment (mentioned below).
[0048]

Exemplary heating maximum temperature in the
thermal ring closure method is 100-500°C, preferably 200-
480°C. When the heating maximum temperature is lower
than the range, sufficient ring closure is difficult to
achieve, and when it is higher than this range,
deterioration proceeds and the film easily becomes
brittle. As a more preferable embodiment, a two-step
heat treatment comprising a treatment at 150-250°C for 3-
20 min, followed by a treatment at 350-500°C for 3-20 min
can be mentioned.
[0049]

According to the chemical ring closure method, a
polyamide acid solution is applied to a support, and an
imidation reaction is partly progressed to form a self-
supporting film, which is followed by heating to
complete the imidation. In this case, the conditions to
partly progress the imidation reaction is a heat
treatment at preferably 100-200°C for 3-20 min, and the
conditions to complete the imidation reaction is a heat
treatment at preferably 200-400°C for 3-20 min.
[0050]

The timing of addition of the ring closing catalyst
to the polyamide acid solution is not particularly
limited, and it may be previously added prior to the
polymerization reaction to give polyamide acid. Specific
examples of the ring closing catalyst include aliphatic
tertiary amine such as trimethylamine, triethylamine and
the like, heterocyclic tertiary amine such as
isoquinoline, pyridine, β-picoline and the like. Of

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these, at least one kind of amine selected from heterocyclic tertiary amine is preferable. While the amount of the ring closing catalyst to be used is not particularly limited, it is preferably 0.5-8 mol per 1 mol of polyamide acid.

[0051]

The timing of the addition of a dehydrating agent to a polyamide acid solution is not particularly limited, and it may be added in advance before a polymerization reaction to obtain polyamide acid. Specific examples of the dehydrating agent include aliphatic carbonic acid anhydrides such as acetic anhydride, propionic acid anhydride, butyric acid anhydride and the like, aromatic carbonic acid anhydrides such as benzoic acid anhydride and the like, and the like. Of these, acetic anhydride, benzoic acid anhydride and a mixture thereof are preferable. While the amount of the dehydrating agent to be used is not particularly limited, it is preferably 0.1-4 mol per 1 mol of polyamide acid. When a dehydrating agent is used, a gelation retardant such as acetylacetone and the like may be used in combination.

[0052]

Whether a thermal ring closure reaction or a chemical ring closure method, a precursor (green sheet, film) of a polyimide film formed on a support may be peeled off from the support before complete imidation or after imidation.

[0053]

The polyimide film of the present invention has a planar orientation coefficient of the film of 0.79-0.89, as measured by the X-ray diffraction method, and a dielectric constant at 100 GHz of the film of 2.7-3.1, as measured by a cavity resonance perturbation method. In addition, it is a polyimide film showing an amount of

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water evaporated at a high temperature of not more than 5000 ppm. Moreover, the absolute value of the difference between the surface planar orientation degree of one surface (surface A) of the film and that of the other surface (surface B) is 0-2.

[0054]

<Planar orientation coefficient of film>

The film of the present invention has a planar orientation coefficient of 0.79-0.89, as measured by the X-ray diffraction method. When the planar orientation coefficient of the film is less than 0.79, the dielectric loss tangent of the film becomes high, which renders it unsuitable for use at a high frequency.

The planar orientation coefficient is a parameter for expressing the higher-order structure of the molecule constituting the film. It numerically expresses the level of orientation, to the film surface, of a particular lattice surface of the crystal lattice, which is a constituent unit of a crystal part having a high orderliness of the molecules constituting the film. A higher value thereof means a smaller difference between the orientation of the aforementioned particular lattice surface and the orientation of the film surface. In the polyimide film of the present invention, "a particular lattice surface" means a lattice surface showing a diffraction peak near $2\theta=21.8°$. The concrete measurement operation of the planar orientation coefficient of the film is described in Examples.

[0055]

In general, as a means for controlling the planar orientation coefficient of the film, adjustment of temperature rise profile during green film forming, stretching during imidation and the like can be mentioned, and the above-mentioned means are applicable to the film of the present invention. For example, to

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make the planar orientation coefficient of the polyimide film higher, a means of reducing the amount of heat to be applied to the green film, and a means of stretching the film in the longitudinal direction, the transverse direction, or both the longitudinal and transverse directions during an imidation reaction can be mentioned. Conversely, to lower the planar orientation coefficient of the polyimide film, a means of increasing the amount of heat to be applied to the green film can be mentioned. Depending on the heating conditions during imidation of the polyimide precursor (polyamide acid), the present inventors can control the planar orientation coefficient of the obtained film. As a preferable means to control the planar orientation coefficient of the film, the heating conditions during imidation can be mentioned. For example, the following heating conditions for imidation reaction are preferable:

method of imidation: two-step heat treatment by thermal ring closure method,

first step heat treatment: treatment at 150-250°C for 1-10 min,

second step heat treatment: treatment at 400-600°C for 0.1-15 min,

temperature rise conditions from the completion of the first step heat treatment to the start of the second step heat treatment: 2-7°C/sec.

[0056]

<Film density>

The film of the present invention preferably has a density of 1.47-1.55 g/cm^3, as measured by the density gradient column method. When the film density is less than 1.47, the dielectric constant of the film becomes high, which is unsuitable for use at a high frequency. A concrete measurement operation of the film density is described in the Examples.

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[0057]

As a means to control the film density, the residual amount of the solvent in the green film may be increased, stretching may be applied during imidation, and the like, and the above-mentioned means are applicable to the film of the present invention. For example, to increase the density of the polyimide film, a means of reducing the amount of heat to be applied to the green film, and a means of stretching the film in the longitudinal direction, the transverse direction, or both the longitudinal and transverse directions during an imidation reaction can be mentioned. Conversely, to lower the density of the polyimide film, a means of increasing the amount of heat to be applied to the green film can be mentioned. Moreover, the present inventors have obtained a new finding that annealing of a polyimide precursor (polyamide acid) before the imidation treatment enables control of the density of the obtained film. As a preferable means to control the film density, annealing before an imidation treatment can be mentioned. For example, the following conditions for annealing before imidation reaction treatment are preferable:

method of annealing before imidation: one-step annealing treatment,

annealing treatment: treatment at 120-150°C for 1-10 min,

temperature rise conditions: 0.5-3°C/sec.

[0058]

<Dielectric property of film>

The film of the present invention as mentioned above shows a small dielectric constant at high frequency and is suitable for use at high frequency. The dielectric constant of the film is defined relative to the signals entering the film surface direction. From

the aspect of applicability at high frequency, a smaller dielectric constant of the film is preferable. A smaller lower limit of the dielectric constant is preferable from the aspect of high frequency characteristics.

5 However, when a dielectric constant of the polyimide film is not more than a given range, other physical properties, particularly mechanical property, are strikingly degraded, which is practically unpreferable. The film of the present invention dielectric constant is

10 2.60-3.00 at 100 GHz, as measured by a cavity resonance perturbation method. It is preferably 2.65-2.90, more preferably 2.70-2.80. The dielectric constant of the film of the present invention at 1 GHz is preferably 2.70-3.10, as measured by a cavity resonance

15 perturbation method. It is preferably 2.75-3.00, more preferably 2.80-2.90.

The dielectric loss tangent of the film of the present invention at 100 GHz is preferably small, not more than 0.01 is preferable, not more than 0.003 is

20 more preferable, and not more than 0.001 is further preferable. While the lower limit of the dielectric loss tangent is not particularly determined, from the aspect of film production, for example, 0.0001 can be mentioned. In the present invention, the dielectric

25 constant and dielectric loss tangent of the film are measured by a cavity resonance perturbation method. Concrete measurement operation is described in the Examples.

[0059]

30 The present inventors have newly found that the dielectric property of the film can be controlled by controlling the density and planar orientation coefficient of the polyimide film. As other means capable of controlling the dielectric of the film, a

35 method of controlling the ratio of a compound remaining

as polyamide acid in the film without imidation
(hereinafter to be also referred to as "ratio of
unreacted polyamide acid") can be mentioned. For
example, to increase the dielectric constant of the
polyimide film, a means of increasing the ratio of
unreacted polyamide acid can be mentioned. Conversely,
to lower the dielectric constant of the polyimide film,
a means of reducing the ratio of unreacted polyamide
acid can be mentioned. As a means to control a
dielectric loss tangent of the film, a means of
controlling the ratio of a compound remaining as
polyamide acid in the film without imidation
(hereinafter to be also referred to as "ratio of
unreacted polyamide acid") or controlling the film
density can be mentioned. For example, to lower the
dielectric loss tangent of the polyimide film, a means
of decreasing the ratio of unreacted polyamide acid or
increasing the film density can be mentioned.
[0060]
<Humidity dependency of dielectric constant>

The polyimide film of the present invention
preferably shows a ratio $\varepsilon_{65}/\varepsilon_D$ within the range of 1.00–
1.10, of the dielectric constant ε_{65} at 100 GHz of the
humidity-conditioned film under the constant temperature
and humidity conditions of 20°C, 65% RH for 94 hr, as
measured by a cavity resonance perturbation method, to
the dielectric constant ε_D at 100 GHz of the film vacuum
dried under the conditions of 120°C, 24 hr, as measured
by a cavity resonance perturbation method. With this
range, a substrate for an electronic circuit substrate
with low humidity dependency and high reliability can be
obtained. As a means to achieve this range, for example,
a method of reducing the amount of water evaporated from
the film at a high temperature can be mentioned
(mentioned later).

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[0061]

<Amount of water evaporated at high temperature>

Being maintained under an inert gas atmosphere at 170°C for 7 min for preliminary drying and then heated at 500°C for 10 sec, the polyimide film of the present invention preferably shows the amount (ppm) of water evaporated during heating at 500°C for 10 sec as mentioned above relative to the polyimide film before preliminary drying (in the present specification, hereinafter sometimes to be abbreviated as "the amount of water evaporated at a high temperature") of not more than 10000 ppm. It is more preferably not more than 7000 ppm, more preferably not more than 4000 ppm, and particularly preferably not more than 2500 ppm.

When the amount of water evaporated at a high temperature is greater than 10000 ppm, the swelling of the polyimide film due to the development of void and the like becomes too high, which easily develops a contact failure caused by delamination.

While a smaller "amount of water evaporated at a high temperature" is more preferable, in consideration of easiness of production, cost and the like, it only needs to be at a level free of substantial inconvenience and the concrete lower limit thereof is not less than 10 ppm. A concrete measurement operation of "the amount of water evaporated at a high temperature" is described in the Examples.

[0062]

To obtain a polyimide film with a small amount of water evaporated at a high temperature, in both the thermal ring closure method and the chemical ring closure method, a heat treatment with a temperature profile by dwelling in a temperature range of not less than 400°C for not less than 5 min is necessary, and the temperature profile is preferably by dwelling in a

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temperature range of 400°C-430°C for not less than 20 min, more preferably dwelling in a temperature range of 430-460°C for not less than 10 min, further preferably dwelling in a temperature range of 460-500°C for not less

5 than 5 min. By a heat treatment of a green film with such temperature profile, the imidation reaction can be carried out to achieve an amount of water evaporated at a high temperature of not more than a given range. While the upper limits of the temperature and time of the

10 temperature profile are not particularly restricted, to avoid decomposition of the film, the temperature is not more than 600°C, preferably not more than 550°C and, in consideration of the producibility, the time is not more than 60 min, preferably not more than 40 min, further

15 preferably not more than 30 min.

[0063]

<Curling degree>

The polyimide film of the present invention is an about flat film made of polyimide obtained by

20 polycondensation of aromatic diamines and aromatic tetracarbonic acid anhydrides, and preferably has a curling degree of not more than 5%. It is possible to have unprecedented superior thermal degradation stability. A concrete measurement operation of the

25 curling degree of a film is described in the Examples.

[0064]

<Difference in the surface planar orientation degree between one surface and the other surface>

In the polyimide film of the present invention, the

30 difference in the surface planar orientation degree between one surface and the other surface is preferably 0-2, more preferably 0-1.5, further preferably 0-1.

When the difference in the surface planar orientation degree between the front and the back of the

35 polyimide film is too large, the difference in the

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stress present in the film between the front and the back becomes large, which is considered to develop curling upon heating treatment and the like. In the present invention, by controlling the difference in the surface planar orientation degree to not more than 2, the thermal degradation stability suitable for a carrier tape for FPC, TAB and the like, as evidenced by the curling degree of the polyimide film of not more than 5%, can be achieved. A concrete measurement operation of the difference in the surface planar orientation degree between one surface and the other surface is described in the Examples. The difference in the surface planar orientation degree between one surface and the other surface is represented by the absolute value of difference, which is obtained by the measurement of the surface planar orientation degree for the front and the back of the polyimide film of the present invention.

[0065]

In the polyimide film of the present invention, the surface planar orientation degree of the surface having a higher surface planar orientation degree is preferably not more than 15, more preferably not more than 10. In the polyimide film of the present invention, when the surface planar orientation degree of the surface having a higher surface planar orientation degree is higher than 15, the difference in the surface planar orientation degree between the front and the back of the film cannot be easily adjusted to a given range, and the film is susceptible to thermal degradation due to a heat treatment (e.g., not less than 300°C).

In the polyimide film of the present invention, while the lower limit of the surface planar orientation degree of the surface having a higher surface planar orientation degree is not particularly limited, from the aspect of the planarity of the film, it is preferably

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not less than 1, more preferably not less than 3 and further preferably not less than 7.5.
[0066]

In step (b), since the direction of evaporation of the solvent during drying of the green film to achieve self-supportedness is limited to the surface in contact with the air, the surface planar orientation degree of the surface of the green film in contact with the air (hereinafter to be also referred to as surface A) tends to be higher than the surface planar orientation degree of the surface in contact with the support (hereinafter to be also referred to as surface B). To obtain a polyimide film showing the difference in the surface planar orientation degree between the front and the back of the film of not more than 2, it is important to obtain a green film showing a small difference in the surface planar orientation degree between the front and the back. For this end, for example, a support is coated with a polyamide acid solution, and the conditions for drying to give a self-supporting green film is controlled, whereby a green film showing a small difference in the surface planar orientation degree between the front and the back can be obtained.

Such difference in the surface planar orientation degree between the front surface and the back surface of the green film is preferably not more than 1.7, more preferably not more than 1.5, further preferably not more than 1. When the difference in the surface planar orientation degree between the front surface and the back surface of the green film exceeds 1.7, the difference in the surface planar orientation degree between the front surface and the back surface of the polyimide film may not be controlled to not more than 2.
[0067]

By controlling the amount of the residual solvent

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relative to the total mass after drying, during drying a
green film to achieve self-supportedness, a green film
showing the difference in the surface planar orientation
degree between the front surface and the back surface
5 within a given range can be obtained. To be specific,
the amount of the residual solvent relative to the total
mass after drying is preferably 25-50% by mass, more
preferably 35-50% by mass. When the amount of the
residual solvent is lower than 25% by mass, the surface
10 planar orientation degree of surface A of the green film
becomes relatively high, which makes it difficult to
obtain a green film showing a small difference in the
surface planar orientation degree between the front
surface and the back surface. In addition, due to the
15 decreased molecular weight, the green film tends to be
brittle. When it exceeds 50% by mass, the self-
supportedness becomes insufficient, and the transport of
the film may become difficult. The amount of the
residual solvent can be measured (calculated) by TGA
20 (thermogravimetric analysis) and the like.
[0068]

    While the thickness of the polyimide film is not
particularly limited, in consideration of use as a base
substrate for the below-mentioned printed wiring
25 assembly, it is generally 1-150 μm, preferably 3-50 μm.
The thickness can be easily controlled by the amount of
a polyamide acid solution to be applied to a support,
and the concentration of the polyamide acid solution.
[0069]

30   The polyimide film obtained by the above-mentioned
production method is wound with the surface having a
higher surface planar orientation degree facing inside
to give a tubular product, whereby a polyimide film
having a smaller curling degree can be obtained.

35   When the film is wound with the surface having a

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higher surface planar orientation degree facing inside
to give a tubular product, its radius of curvature is
preferably within the range of from 30 mm to 300 mm.
When the radius of curvature exceeds this range, the
5   curling degree of the polyimide film may become greater.
[0070]

        Now, a base substrate for a printed wiring assembly
comprising the aforementioned polyimide film is
explained.
10   As used herein the "base substrate for a printed
wiring assembly" is an about planar substrate comprising
an insulating plate and a metal layer laminated on at
least one surface of the plate. The metal layer to be
laminated may be one for a circuit intended to form a
15   circuit by a processing such as etching and the like.
Alternatively, it may be a metal layer used for
releasing heat and the like without a particular post-
processing, together with an insulating plate.
        As the use of "a base substrate for a printed
20   wiring assembly", FPC, a carrier tape for TAB, a
substrate for COF, a substrate for CSP and the like are
preferable, since the characteristic of small curling
degree of the polyimide film of the present invention
can be utilized.
25   [0071]

        The metal to be laminated on at least one surface
of the polyimide film is not particularly limited, and
is preferably copper, aluminum, stainless steel and the
like. The laminating means is not particularly limited
30   and the following means can be exemplified:
·means of adhering a metal plate to a polyimide film
with an adhesive,
·means of forming a metal layer on a polyimide film by a
vacuum coating technique such as vapor deposition,
35   sputtering, ion plating and the like,

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·means of forming a metal layer on a polyimide film by
wet plating method such as electroless plating,
electroplating and the like.

These means can be used alone or in combination to
laminate a metal layer on at least one surface of a
polyimide film.
[0072]

Of these, as a method for laminating a metal layer,
a method comprising forming an underlaying metal layer
by sputtering and thickening by electroplating is a
particularly preferable embodiment.

In this case, as the underlaying metal, a single
metal or alloy of Cu, Ni, Cr, Mo, Zn, Ti, Ag, Au, Fe and
the like can be used. In addition, a good conductor such
as Cu and the like may be attached as a conductive layer
to an underlying metal by sputtering.

The thickness of the underlayer and conductive
layer is preferably 100-5000 Å.

As a metal to be electroplated, Cu is preferable.
[0073]

While the thickness of the metal layer is not
particularly limited, when the metal layer is used for a
circuit (conductive), the thickness of the metal layer
is preferably 1-175 μm, more preferably 3-105 μm. When a
polyimide film adhered with a metal layer is used as a
heat release substrate, the thickness of the metal layer
is preferably 50-3000 μm. While the roughness of the
surface to be adhered to polyimide of the metal layer is
not particularly limited, metal layers showing Ra of not
more than 0.1 μm and Rz of not more than 1.00 μm are
preferable, according to JIS B 0601 (Definition and
Designation of Surface Roughness) based on the center
line average roughness (hereinafter indicated as Ra) and
10 points average roughness (hereinafter indicated as
Rz), since the metal layers afford a greater improving

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effect on the adhesion to the metal layer. Of such metal layers, one simultaneously satisfying the conditions is particularly preferable. While smaller Ra and Rz are more preferable, the lower limit of Ra is 0.0001 μm and, for example, the lower limit of Rz is 0.001 μm, due to the easiness of obtaining and processing.

[0074]

The metal layer to be used in the present invention may have, on its surface, a coating film of inorganic materials of a single metal, metal oxide and the like. In addition, the surface of the metal layer may be subjected to a treatment with a coupling agent (aminosilane, epoxysilane and the like), a sandblast treatment, a honing treatment, a corona treatment, a plasma treatment, an etching treatment and the like. Similarly, the surface of the polyimide film may be subjected to a honing treatment, a corona treatment, a plasma treatment, an etching treatment and the like.

Examples

[0075]

The effectiveness of the present invention is explained in the following by referring to Examples, which are not to be construed as limitative. In the following Examples, the evaluation methods of the properties are as follows.

1. Reduced viscosity (ηsp/C) of polyamide acid

A solution of a polymer in N-methyl-2-pyrrolidone to a polymer concentration of 0.2 g/dl was measured with a Uberode type viscosity tube at 30°C.

2. Film thickness of polyimide film

The film thickness was measured with a micrometer (Millitron (R)1245D, manufactured by Finepruf).

3. Tensile elastic modulus, tensile strength at break and tensile elongation at break of polyimide film

A film after drying was cut out in the longitudinal

direction (MD direction) and transverse direction (TD direction) to give a reed-shaped strip (length 100 mm, width 10 mm) as a test piece, which was subjected to the measurement of tensile elastic modulus, tensile strength at break and tensile elongation at break using a tensile test machine (AUTOGRAPH (R), model AG-5000A, manufactured by Shimadzu Corporation) at a tensile rate of 50 mm/min and a chuck distance of 40 mm.

[0076]

4. Coefficient of linear thermal expansion of polyimide film (CTE)

The rate of expansion and contraction was measured under the following conditions, wherein 30-300°C was divided by 15°C and CTE was determined from the average of rate of expansion and contraction of each divided range/temperature.

name of apparatus: TMA4000S manufactured by MAC SCIENCE

sample length: 20 mm

sample width: 2 mm

temperature rise start at: 25°C

temperature rise end at: 400°C

rate of temperature rise: 5°C/min

atmosphere: argon

[0077]

5. Melting point and glass transition temperature of polyimide film

The sample was subjected to DSC measurement under the following conditions and the melting point (melting peak temperature Tpm) and the glass transition temperature (Tmg) were determined under the following measurement conditions according to JIS K 7121.

name of apparatus: DSC3100S manufactured by MAC SCIENCE

pan: aluminum pan (non-airtight type)

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sample mass: 4 mg

temperature rise start at: 30°C

rate of temperature rise: 20°C/min

atmosphere: argon

[0078]

6. Thermal decomposition temperature of polyimide film

The thermal decomposition temperature was defined by subjecting a fully dried sample to TGA measurement (thermobalance measurement) under the following conditions, and measuring 5% mass reduction.

name of apparatus: TG-DTA2000S manufactured by MAC SCIENCE

pan: aluminum pan (non-airtight type)

sample mass: 10 mg

temperature rise start at: 30°C

rate of temperature rise: 20°C/min

atmosphere: argon

[0079]

7. Planar orientation coefficient of the polyimide film

A measurement target polyimide film was set on a measurement jig, X-ray diffraction measurement was performed under the following conditions, and a pole figure of the diffraction peaks appearing near $2\theta=21.8°$ was drawn.

name of apparatus: RINT 2100PC manufactured by Rigaku Corporation, multipurpose sample table

voltage, electric current: 40 kV, 40 mA

measurement methods: reflection method and through method

scanning range: reflection method

α; 15-90°/2.5° intervals

β; 0-360°/5° intervals

reflection method

α; 0-15°/2.5° intervals

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β; 0-360°/5° intervals

slit: DS 0.1 mm, SS 7 mm, RS 7 mm,

longitudinal divergence limiting slit 1.2 mm

scanning speed: continuous (360°/min)

5   detector: scintillation counter

Fig. 1 schematically shows the pole figure. In the
Figure, peak half-width (HMD and HTD) was determined
from the diffraction strength profile at two broken
lines, and an average value of HMD and HTD was defined

10 as Ha (unit:°). The peak half-width was determined using
the analysis programs manufactured by Rigaku. The planar
orientation coefficient of the polyimide film was
calculated from the thus-obtained Ha by the following
formula:

15   planar orientation coefficient = (180° − Ha)÷180°

[0080]

8. Difference in the surface planar orientation degree
of polyimide film

The surface planar orientation degree was measured

20 using polarized ATR and at incident angle 45°,
decomposability 4 cm^{-1} and number of integration 128
times. The absorption coefficient (Kx) in the MD
direction, absorption coefficient (Ky) in the TD
direction and absorption coefficient (Kz) in the

25 thickness direction at the peak (aromatic ring
oscillation) near 1480 cm^{-1} were determined for each of
the front and the back of the polyimide film, and the
surface planar orientation degree was calculated from
the following formula:

30 surface planar orientation degree=(Kx+Ky)/2×Kz

In addition, the difference in the surface planar
orientation degree between the front and the back of the
polyimide film of the present invention is, as shown in
the following formula, calculated from the absolute

35 value of the difference in the surface planar

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orientation degree between the surface on the air side (surface A) and the surface on the support side (surface B):

difference in the surface planar orientation degree = |surface planar orientation degree of surface A - surface planar orientation degree of surface B|

name of apparatus: FT-IR (FTS-60A/896 manufactured by Digilab)

one time reflection ATR attachment: golden gate MKII (manufactured by SPECAC)

IRE: diamond

incident angle: 45°

[0081]

9. Curling degree of polyimide film

A 50 mm×50 mm test piece was set on an alumina-ceramic flat board, hot air treated at 400°C for 10 min and then a curling degree was calculated from the following formula wherein an average value of the distance (h_1, h_2, h_3, h_4: unit mm) from the ceramic boards on four corners was taken as a curl amount (mm). The curl amount of the ceramic board itself used is not more than 0.1 mm.

curl amount (mm) = (h_1+h_2+h_3+h_4)/4

curling degree (%) = 100 × (curl amount, mm)/35.36 mm

[0082]

10. Volume resistivity of polyimide film

Using the method according to JIS C2318, the volume resistivity was measured.

11. Dielectric breakdown voltage of polyimide film

Using the method according to JIS C2318, the dielectric breakdown voltage was measured.

[0083]

12. Dielectric constant of polyimide film

(Preparation of test piece)

The polyimide films in the number necessary to

40

afford a desired thickness were placed on top of one another, pressed with a load of 300 kgf/cm^2 to give a 1.6 mm×1.5 mm×75 mm rectangular columnar test piece. (Measurement of test piece)

5   Using a N5250A milliwave PNA Series Network Analyzer manufactured by Agilent Technologies, the dielectric constant and dielectric loss tangent within the range of 1 GHz - 100 GHz were measured and recorded for the above-mentioned sample according to the cavity
10   resonance perturbation method.

Using the rectangular columnar test piece, a dry sample and a humidity-conditioned sample were prepared as follows. The dry sample was obtained by vacuum drying a rectangular columnar test piece at 120°C for 24 hr. In
15   addition, the humidity-conditioned sample was obtained by humidity-conditioning a rectangular columnar test piece under constant temperature and humidity conditions at 20°C, 65%RH for 94 hr. The dielectric property measurement was performed immediately after completion
20   of drying or humidity-conditioning, or the dry or humidity-conditioned film state was maintained by preserving in an aluminum sack under a nitrogen atmosphere until the dielectric property measurement. (Measurement of test piece)

25   Using a N5250A milliwave PNA Series Network Analyzer manufactured by Agilent Technologies, the dielectric constant and dielectric loss tangent within the range of 1 GHz - 100 GHz were measured and recorded for the above-mentioned humidity-conditioned sample
30   according to the cavity resonance perturbation method. In Examples 5, 6 and Comparative Examples 4, 5, the dielectric constant and dielectric loss tangent at 100 Hz were also measured and recorded for a dry sample.
[0084]

35   13. Density of polyimide film

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A polyimide film was cut out into a 5 mm×5 mm size and subjected to a density measurement. The sample thus cut out was cast into a density gradient tube prepared with a aqueous calcium nitrate solution, and the density was measured from the position of a standard float previously set therein, whose density had been known, an analytical density curve and the position of the sample after 5 hr. The liquid temperature of the density gradient tube was 30°C.

[0085]

14. Measurement method of the amount of residual solvent in polyimide precursor film

Using a TGA apparatus (TG-DTA2000S manufactured by MAC SCIENCE), heat mass decrease of a polyimide precursor film subjected to temperature rise from room temperature to 400°C at 10°C/min in a nitrogen stream and maintained at 400°C for 30 min was measured. The mass decrease rate was taken as the amount of the residual solvent (% by mass) assuming that all the mass decrease was caused by evaporation of the residual solvent.

[0086]

15. Content of water evaporated from polyimide film at high temperature

Using a Curie-point type thermal decomposition device and according to the GCMS method, the amount of evaporated water was determined.

A sample (roughly 8 mg) was precisely measured (basis weight A (mg)) in a pyrofoil for 500°C (manufactured by Japan Analytical Industry Co., Ltd.) dried in advance by heat treatment. An incubation temperature in the thermal decomposition device was set to 170°C, the sample foil was introduced thereinto, purged with helium for 7 min and water adsorbed to the film was removed by preliminary drying. Then, the film was immediately heated by oscillation operation at 500°C

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for 10 sec. As regards the water evaporated from the film during heating at 500°C for 10 sec, water ion peak at $m/z=18$ was detected by GCMS. The peak area was measured and developed water content B (μg) was
5 determined by the absolute analytical curve method. The analytical curve was formed from the peak area of a standard solution containing not less than two levels of a given amount of water, which was prepared using, as a preparation reagent, dry methanol over anhydrous sodium
10 sulfate, at $m/z=18$ by GCMS. The analytical curve was $y=ax+b$ (a: slope, b: intercept, y: developed water content B (μg), x: peak area). The amount of water evaporated from the polyimide film at a high temperature was calculated from the following formula.

15   the amount of water evaporated at a high temperature (ppm)=B (μg)/(A (mg)×1000)
        thermal decomposition GCMS conditions
        apparatus: HP5971A (GCMS manufactured by HP), JHS-3 (thermal decomposition device manufactured by Japan
20 Analytical Industry Co., Ltd.)
        column: PORAPLOT-Q (manufactured by GL Sciences
                Inc.), $\phi 0.32$ mm × 10 m
        column temperature: 60°C constant
        flow rate: He 0.7 ml/min, split injection

25 [0087]
16. Solder heat resistance and contact failure rate of polyimide film
<Preparation of adhesive>
        As an adhesive, (A) polyamide resin (acid
30 component: dimer acid, amine component: hexamethylenediamine, acid value 1.0, amine value 0), (B) epoxy resin I: 4,4'-bis(2,3-epoxypropoxy)-3,3',5,5'-tetramethylbiphenyl (epoxy equivalent amount: 190) (C) epoxy resin II. bisphenol A type epoxy resin (epoxy
35 equivalent amount: 186), (D) phenol resin

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resolphenol "CKM-1282" (manufactured by SHOWA HIGHPOLYMER CO., LTD.), and (E) additive 2-heptadecylimidazole were mixed at a ratio of 50.0:8.0:12.0:29.5:0.5 (mass ratio) and used.

[0088]

<Production of buildup multi-layer wiring board>

A 4 layer print wire board of FR4 was used as a core layer, and the buildup multi-layer printed wire boards shown in Figs. 3, 4 were preproduced. The thickness of the copper foil on the surface of the core layer was 25 μm. An adhesive solution was first applied to one surface of the polyimide film and dried at 80°C×40 min. The thickness of the dry film of the adhesive was 25 μm. Then, a polyimide film having an adhesive applied to the both surfaces of the core substrate was superimposed, tentative pressed with a vacuum laminater, and then pressed with a hot plate press heated to 150°C at actual weight of 20 kgf/cm^2 for 30 min. A YAG laser was used for perforation. The via diameter was 150 μm. After perforation, a desmear treatment was performed. After washing with water, the entire surface of the substrate was plasma-treated and, after conditioning, catalyst addition and activation, 0.8 μm thick electroless copper plating was applied in a formalin reduction bath, electroplating for thickening and via fill plating were performed in a sulfuric acid copper plating bath, and the surface was buffed to ensure planarity, at which point the thickness of the copper foil was 15 μm. For formation of a pattern, a 25 μm thick dry film resist was laminated, exposed to light, developed and etched with a cupric chloride solution, then the resist was peeled off, and the substrate was washed with dilute sulfuric acid to give a conductor pattern with a thin line width of 70 μm.

[0089]

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<Solder heat resistance>

The second buildup layer was formed in the same manner as in the first buildup layer except that the adhesive to be applied to the polyimide film was 15 μm thick. By the above-mentioned steps, a multi-layer printed wire board having a total of 8 layers, with two buildup layers on each side, was obtained.

The obtained multi-layer printed wire board was immersed for 10 sec in a tin-copper-silver, lead-free solder tank heated to 280°C, and the presence or absence of peeling, swelling and the like was visually observed.

Then, the board was set on an ETAC (R) temperature cycle test apparatus (manufactured by Kusumoto Chemicals, Ltd.) and a heating-cooling cycle test wherein the board was heated and cooled every 30 min between a low temperature of -50°C and a high temperature of 150°C was performed for 100 hr. After the test, the board was immersed for 10 sec in a tin-copper-silver lead-free solder tank heated to 280°C, and the presence or absence of peeling, swelling and the like was visually observed.

[0090]

<Contact failure rate>

A 7 mm × 7 mm semiconductor chip was mounted on the obtained multi-layer printed wire board (25.4 mm × 25.4 mm) by face-down bonding. The number of bondings was 256.

The package was set on an ETAC (R) temperature cycle test apparatus (manufactured by Kusumoto Chemicals, Ltd.) and a heating-cooling cycle test wherein the board was heated and cooled every 30 min between a low temperature of -50°C and a high temperature of 150°C was performed for 500 hr. After the test, the board was subjected to a conduction test, and a connection point failure rate was determined.

45

[0091]

(Examples 1-4, Comparative Examples 1-3)

<Production Example of polyamide acid solution - 1>

A reaction container equipped with a nitrogen inlet tube, a thermometer and a stirring rod was purged with nitrogen, and 500 parts by mass of 5-amino-2-(p-aminophenyl)benzoxazole was placed therein. Then, 9000 parts by mass of N-methyl-2-pyrrolidone was added and, after complete dissolution, 485 parts by mass of pyromellitic acid dianhydride was added. The mixture was stirred at 25°C for 50 hr to give a brown viscous polyamide acid solution. The reduced viscosity (ηsp/C) was 4.6 dl/g.

<Production Example of film - 1>

The polyamide acid solution was applied to a stainless belt (squeegee/belt gap was 650 μm) and dried at 90°C for 60 min. After drying, a self-supporting polyamide acid film was peeled off from a stainless belt to give a green film having a thickness of 40 μm.

The obtained green film was passed through a nitrogen purged continuous type heat treatment furnace, and heated in two steps under the conditions described in Table 1 to carry out an imidation reaction. Thereafter, the film was cooled to room temperature over 5 min to give brown polyimide films of Examples 1-4 and Comparative Examples 1-3. The evaluation results of each polyimide films obtained are shown in Table 1.

[0092]

Table 1

			Ex.1	Ex.2	Ex.3	Ex.4	Com. Ex.1	Com. Ex.2	Com. Ex.3
annealing conditions before imidation reaction treatment	temperature	°C	130	130	150	150	170	–	130
	time	min	5	4	3	1	2	–	0.5
imidation conditions	first step	temperature rise °C/min	1.0	0.6	1.5	1.3	1.8	–	0.7
	first step	temperature °C	200	170	200	170	200	170	130
	first step	time min	4	6	4	5	3	5	4
	temperature rise	°C/min	5	3	5	4	5	3	2
	second step	temperature °C	500	450	450	450	450	380	450
	second step	time min	2	7	6	5	5	10	5
thickness		μm	25	25	25	25	25	25	25
tensile elastic modulus	MD	GPa	9	8.2	8	7.9	7.5	6.6	6.2
	TD	GPa	9	8	7.9	7.9	7.2	6.5	6.1
tensile strength at break	MD	MPa	400	360	370	350	350	310	280
	TD	MPa	390	350	360	340	310	290	250
tensile elongation at break	MD	%	25	28	29	32	30	47	58
	TD	%	24	26	28	30	27	44	55
coefficient of linear thermal expansion	MD	ppm/°C	5	8	8	10	12	17	24
	TD	ppm/°C	4	6	7	8	10	15	20
melting point		°C	none	none	none	none	none	none	none
glass transition temperature		°C	none	none	none	none	none	none	none
thermal decomposition temperature		°C	620	610	600	590	610	590	590
planar orientation coefficient		-	0.87	0.83	0.82	0.79	0.81	0.78	0.75
density		g/cm³	1.53	1.51	1.49	1.48	1.46	1.46	1.45
volume resistivity×10^{-16}		Ωcm	2.0	1.8	1.6	1.3	1.0	0.9	0.9
dielectric breakdown voltage		KV	6.5	6.8	6.3	6.1	5.2	4.3	3.8
dielectric constant (ε_{65})	1 GHz	-	2.8	2.9	3.1	3.1	3.2	3.2	3.3
	10 GHz	-	2.7	2.8	3.0	3.0	3.0	3.1	3.2
	100 GHz	-	2.7	2.8	2.9	3.0	3.0	3.1	3.2
dielectric loss tangent	1 GHz	-	0.006	0.007	0.012	0.015	0.043	0.060	0.060
	10 GHz	-	0.004	0.005	0.010	0.011	0.036	0.051	0.053
	100 GHz	-	0.001	0.003	0.006	0.008	0.032	0.040	0.045

MD: longitudinal direction (machine direction)   TD: transverse direction

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[0093]

(Example 5)

<Production Example of polyamide acid solution - 2>

        A reaction container equipped with a nitrogen inlet
tube, a thermometer and a stirring rod was purged with
nitrogen, and 5-amino-2-(p-aminophenyl)benzoxazole
(formula 1, 450 parts by mass) and 5-amino-2-(m-
aminophenyl)benzoxazole (formula 3, 50 parts by mass)
were placed therein. Then, 9100 parts by mass of N,N-
dimethylacetamide was added and, after complete
dissolution, 485 parts by mass of pyromellitic acid
dianhydride was added. The mixture was stirred at 25°C
for 40 hr to give a brown viscous polyamide acid
solution A. The ηsp/C thereof was 4.0 dl/g.

<Production Example of film - 2>

        The polyamide acid solution was applied to a
stainless belt (squeegee/belt gap was 650 μm) and dried
at 90°C for 60 min. After drying, a self-supporting
polyamide acid film was released from a stainless belt
to give a green film having a thickness of 40 μm. The
amount of the residual solvent in the green film then
was 35% by mass.

        The obtained green film was passed through a
continuous type drying furnace, and heat-treated at 170°C
for 3 min, after which the temperature was elevated to
450°C at about 70°C/min, heat-treated at 450°C for 10 min,
cooled to room temperature over 5 min to give a brown
polyimide film having a thickness of 25 μm. The obtained
polyimide film was evaluated for the properties. Using
the obtained polyimide film, a buildup multi-layer
wiring board was produced and the solder heat resistance
and contact failure rate were evaluated. The respective
evaluation results are shown in Table 2.

[0094]

(Example 6)

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In the same manner as in Example 5 except that the temperature profile of the heat treatment was as shown in Table 2, a polyimide film and a buildup multi-layer wiring board were obtained and subjected to similar evaluation. The results are shown in Table 2.

[0095]

(Comparative Examples 4, 5)

<Production Example of polyamide acid solution - 3>

A reaction container equipped with a nitrogen inlet tube, a thermometer and a stirring rod was purged with nitrogen, and 5-amino-2-(p-aminophenyl)benzoxazole (formula 1, 450 parts by mass) and 5-amino-2-(m-aminophenyl)benzoxazole (formula 3, 50 parts by mass) were placed therein. Then, 9100 parts by mass of N-methylpyrrolidone was added and, after complete dissolution, 485 parts by mass of pyromellitic acid dianhydride was added. The mixture was stirred at 25°C for 40 hr to give a brown viscous polyamide acid solution B. The ηsp/C thereof was 4.1 dl/g.

<Production Example of film - 3>

In the same manner as in Example 5 except that the temperature profile of the heat treatment was as shown in Table 2, a polyimide film and a buildup multi-layer wiring board were obtained using the obtained polyamide solution and subjected to similar evaluation. The evaluation results are shown in Table 2.

The solder heat resistance and contact failure of the polyimide films of Examples 5 and 6, wherein the amount of water evaporated at a high temperature was not more than 10000 ppm, were superior. However, in Comparative Examples 1 and 2, swelling was developed in the solder heat resistance test after the heating-cooling cycle test, and the contact failure rate was also high.

[0096]

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Table 2

			Ex. 5	Ex. 6	Com. Ex. 4	Com. Ex. 5
solvent of polyamide acid dope			DMAc	DMAc	NMP	DMAc
amount of residual solvent GF		% by mass	35	32	38	41
heat treatment	temperature at start	°C	170	200	170	200
	temperature rise rate	°C/min	70	60	70	60
	temperature reached	°C	450	480	450	380
	dwelling time	min	10	15	3	30
thickness		μm	25	25	25	25
tensile strength at break	MD	MPa	350	380	290	330
	TD	MPa	340	370	280	310
tensile elastic modulus	MD	GPa	7.8	9.4	4	7.3
	TD	GPa	7.8	9.3	3.8	7
tensile elongation at break	MD	%	32	26	61	49
	TD	%	33	27	57	46
coefficient of linear thermal expansion	MD	ppm	6	3	23	19
	TD	ppm	4	4	21	17
melting point		°C	none	none	none	none
glass transition temperature		°C	none	none	none	none
thermal decomposition temperature		°C	610	623	585	610
amount of water evaporated at high temperature		ppm	4500	2300	12000	23000
ε_D (dry, 100 Hz)		-	2.9	2.7	3.1	3.2
ε_{65} (humidity conditioned, 100 Hz)		-	3.0	2.8	3.5	3.7
$\varepsilon_{65}/\varepsilon_D$		-	1.03	1.04	1.13	1.16
solder heat resistance	after temperature cycle		good	good	swelling occurred	swelling occurred
contact failure rate	after temperature cycle		5.2	4.3	97	0.5

NMP: N-methyl-2-pyrrolidone
MD: longitudinal direction (machine direction)
DMAc: N,N-dimethylacetoamide
TD: transverse direction

[0097]

(Example 7)

<Production Example of polyamide acid solution - 4>

A reaction container equipped with a nitrogen inlet tube, a thermometer and a stirring rod was purged with nitrogen, and 500 parts by mass of 5-amino-2-(p-aminophenyl)benzoxazole was placed therein. Then, 9000 parts by mass of N-methyl-2-pyrrolidone was added and, after complete dissolution, 485 parts by mass of pyromellitic acid dianhydride was added. The mixture was stirred at 25°C for 15 hr to give a brown viscous polyamide acid solution. The ηsp/C thereof was 4.0 dl/g.

[0098]

<Production Example of film - 4>

The polyamide acid solution was applied to a stainless belt (squeegee/belt gap was 650 μm) and dried at 90°C for 60 min. After drying, a self-supporting polyamide acid film was peeled off from a stainless belt to give a green film having a thickness of 40 μm. The amount of the residual solvent in the green film was 39%.

The obtained green film was passed through a continuous type drying furnace, and heat-treated at 170°C for 3 min, after which the temperature was elevated to 450°C at about 70°C/min, the film was heat-treated at 450°C for 10 min and cooled to room temperature over 5 min to give a brown polyimide film having a thickness of 25 μm. The properties of the obtained polyimide film were evaluated. A buildup multi-layer wiring board was produced using the obtained polyimide film, and evaluated for the solder heat resistance and contact failure rate. The respective evaluation results are shown in Table 3.

[0099]

(Example 8, Comparative Examples 6, 7)

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In the same manner as in Example 7 except that the temperature profile of the heat treatment was as shown in Table 3, polyimide films and buildup multi-layer wiring boards were obtained and subjected to similar evaluation. The evaluation results are shown in Table 3.
[0100]

Table 3

		Ex. 7	Ex. 8	Com. Ex. 6	Com. Ex. 7
amount of residual solvent GF	% by mass	39	33	35	42
imidation conditions — temperature at start	°C	170	200	170	200
temperature rise rate	°C/min	70	60	70	60
temperature reached	°C	450	420	450	380
dwelling time	min	10	15	3	30
thickness	μm	25	25	25	25
tensile elastic modulus — MD	GPa	7.9	9.5	4.1	7.5
TD	GPa	7.9	9.4	3.9	7.2
tensile strength at break — MD	MPa	360	370	300	350
TD	MPa	340	360	280	310
tensile elongation at break — MD	%	30	25	58	47
TD	%	31	24	55	44
coefficient of linear thermal expansion — MD	ppm	5	4	24	17
TD	ppm	3	3	20	15
melting point	°C	none	none	none	none
glass transition temperature	°C	none	none	none	none
thermal decomposition temperature	°C	610	625	590	620
amount of water evaporated at high temperature	ppm	4800	2200	12000	23000
solder heat resistance (after temperature cycle)		good	good	swelling occurred	swelling occurred
contact failure rate (after temperature cycle)		5.2	4.3	97	0.5

MD: longitudinal direction (machine direction)   TD: transverse direction

[0101]

(Examples 9-11, Comparative Examples 8-10)

In the same manner as in Example 7 except that the obtained green film was passed through a nitrogen purged continuous type heat treatment furnace, and heated in two steps under the conditions described in Table 4 to carry out an imidation reaction, a polyimide film was obtained and subjected to the evaluation in the same manner. The evaluation results are shown in Table 4.

[0102]

54

Table 4

irradiation conditions				Ex.9	Ex.10	Com.Ex.8	Com.Ex.9	Com.Ex.10
first step	temperature		°C	170	200	170	200	130
	time		min	3	2	3	1	3
temperature rise			°C/min	3	6	0.5	3	2
second step	temperature		°C	450	500	380	380	450
	time		min	7	1	5	10	5
thickness			μm	25	25	25	25	25
tensile elastic modulus		MD	GPa	7.9	9.0	4.1	7.5	6.2
		TD	GPa	7.9	9.0	3.9	7.2	6.1
tensile strength at break		MD	MPa	350	380	300	350	280
		TD	MPa	340	370	280	310	250
tensile elongation at break		MD	%	25	25	58	47	20
		TD	%	24	24	55	44	15
coefficient of linear thermal expansion		MD	ppm	6	5	24	17	12
		TD	ppm	5	4	20	15	10
melting point			°C	none	none	none	none	none
glass transition temperature			°C	none	none	none	none	none
thermal decomposition temperature			°C	610	620	590	620	590
planar orientation coefficient			-	0.82	0.87	0.75	0.78	0.77
volume resistivity			x10^{16}Ωcm	1.5	2.0	0.9	1.0	1.0
dielectric breakdown voltage			KV	6.8	6.5	4.2	3.8	5.1
dielectric constant (ε$_{65}$)		1 GHz	-	3.0	2.8	3.2	3.1	3.2
		10 GHz	-	2.9	2.7	3.0	3.0	3.1
		100 GHz	-	2.8	2.7	2.9	2.9	3.1
dielectric loss tangent		1 GHz	-	0.008	0.006	0.060	0.041	0.060
		10 GHz	-	0.006	0.004	0.058	0.035	0.051
		100 GHz	-	0.002	0.001	0.050	0.032	0.045

MD: longitudinal direction (machine direction)   TD: transverse direction

55

[0103]

(Example 12)

<Preparation Example of polyamide acid solution - 5>

A polyamide acid solution was obtained by a method similar to that in Example 7.

<Production Example of film - 5>

The polyamide acid solution was applied to a stainless belt (squeegee/belt gap was 650 μm) and dried in three hot air type drying zones at 90°C×20 min, 90°C×20 min and 90°C×20 min.

After drying, a self-supporting polyamide acid film was peeled off from a stainless belt to give a green film having a thickness of 40 μm. The obtained green film was passed through a continuous type drying furnace, and heat-treated at 170°C for 3 min, after which the temperature was elevated to 450°C over about 20 seconds, the film was heat-treated at 450°C for 7 min and cooled to room temperature over 5 min to give a brown polyimide film having a thickness of 25 μm. The properties of the obtained polyimide film are shown in Table 5.

[0104]

(Examples 13, 14, Comparative Examples 11-14)

In the same manner as in Example 12 except that a polyamide acid solution was applied to a stainless belt and temperature×time of the three hot air type drying zones was as shown in Table 5, a green film was obtained, which was then heat treated in the same manner as in Example 12 to give a polyimide film.

The property values of the polyimide films of Examples 13 and 14 are shown in Table 5, and the property values of the polyimide films of Comparative Examples 11-14 are shown in Table 6.

[0105]

Table 5

			Ex. 11	Ex. 12	Ex. 13
green film production conditions	temperature-1	°C	90	90	110
	temperature-2	°C	90	100	110
	temperature-3	°C	90	120	110
	time (1-3)	min	20 each	10 each	10 each
amount of residual solvent of GF	% by mass		41.7	35.1	35.3
thickness	μm		24	25	25
tensile elastic modulus	GPa		6.8	6.4	7.2
tensile strength at break	MPa		450	480	500
tensile elongation at break	%		35	31	30
coefficient of linear thermal expansion	ppm		3	2	4
melting point	°C		none	none	none
glass transition temperature	°C		none	none	none
surface planar orientation degree	surface B	–	8.772	8.000	7.813
	surface A	–	9.615	8.929	9.259
difference in surface planar orientation degree |A-B|	–		0.843	0.929	1.446
curling degree	mm		1.0	1.2	1.5
	%		2.8	3.4	4.2

MD: longitudinal direction (machine direction)

TD: transverse direction

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[0106]

Table 6

			Com. Ex.11	Com. Ex.12	Com. Ex.13	Com. Ex.14
green film production conditions	temperature-1	°C	100	130	120	150
	temperature-2	°C	120	130	140	150
	temperature-3	°C	130	130	150	150
	time (1-3)	min	10	10	5	5
amount of residual solvent of GF	% by mass		32.0	30.4	24.7	23.5
thickness	μm		24	25	25	24
tensile elastic modulus	GPa		6.5	5.8	5.5	5
tensile strength at break	MPa		420	350	360	320
tensile elongation at break	%		27	15	12	5
coefficient of linear thermal expansion	ppm		3	15	12	38
melting point	°C		none	none	none	none
glass transition temperature	°C		none	none	none	none
surface planar orientation degree	surface B	-	5.882	4.762	3.704	4.000
	surface A	-	9.091	7.143	6.250	7.692
difference in surface planar orientation degree |A-B|		-	3.209	2.381	2.546	3.692
curling degree	mm		6.0	10.0	>10	>10
	%		17.0	28.0	>28	>28

MD: longitudinal direction (machine direction)

TD: transverse direction

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Industrial Applicability

[0107]

The film of the present invention shows lower loss and faster response speed (good rise of pulse signals) at high frequency as compared to conventionally known polyimide films. Therefore, the film is useful as a substrate film for the production of copper-adhered substrates for flexible print circuit (FPC) used for high frequency electronics, a carrier tape for tape automated bonding (TAB) and the like. In addition, the film shows a small difference in dielectric constant between a dry state and a wet state, the amount of water evaporated at a high temperature is extremely small and the development of swelling and delamination can be prevented when used at a high temperature. Therefore, the film is useful as a substrate film of a substrate used for electronics required to show high reliability.

The polyimide film of the present invention is an unprecedented polyimide film superior in thermal degradation stability, which has a curling degree of not more than 5%, and shows high rigidity, high strength and high heat resistance like the conventional polyimide films. Therefore, the film is preferably used as a substrate film for the production of copper-adhered substrates for flexible print circuit (FPC) with strict dimensional precision requirements, a carrier tape for tape automated bonding (TAB) and the like.

Brief Description of the Drawings

[0108]

Fig. 1 schematically shows an X-ray diffraction pole figure of a polyimide film.

Fig. 2 is a schematic view showing the measurement method of the curling degree of a polyimide film, wherein (a) is a top view, (b) is a sectional view along a-a in (a) before a hot air treatment, and (c) is a

sectional view along a-a in (a) after a hot air treatment.

Fig. 3 is a schematic view showing a step for forming a first buildup layer in the production of a buildup multi-layer wiring board.

Fig. 4 is a schematic view showing a step for forming a second buildup layer in the production of a buildup multi-layer wiring board.

Explanation of Symbols

[0109]

1   test piece of polyimide film

2   alumina-ceramic plate

3   1 core substrate

4   2 core substrate conductor pattern

5   3 adhesive layer

6   4 heat resistant film (polyimide film)

7   5 buildup conductive layer